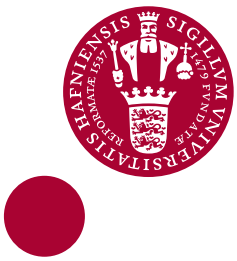

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Large increases in arctic biogenic volatile organic compound emissions are a direct effect of warming

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Biogenic volatile organic compounds are reactive gases that can contribute to atmospheric aerosol formation[1]. Their emission from vegetation is dependent on temperature and light availability[2]. Increasing temperature, changing cloud cover, and shifting composition of vegetation communities can be expected to affect emissions in the Arctic, where the ongoing climate changes are particularly severe[3]. Here we present biogenic volatile organic compound emission data from arctic tundra exposed to six years of experimental warming or reduced sunlight treatment in a randomized block design. By separately assessing the emission response of the whole ecosystem, plant shoots and soil in four measurements covering the growing season, we have identified that warming increased the emissions directly rather than via a change in the plant biomass and species composition. Warming caused a 260% increase in total emission rate for the ecosystem and a 90% increase in emission rates for plants, while having no effect on soil emissions. Compared to the control, reduced sunlight decreased emissions by 69% for the ecosystem, 61-65% for plants and 78% for soil. The detected strong emission response is considerably higher than observed at more southern latitudes, emphasizing the high temperature sensitivity of ecosystem processes in the changing Arctic.

All organisms release VOCs for a range of physiological and ecological reasons, but the majority of emissions is derived from vegetation[2]. When low-volatile BVOC oxidation products condensate onto aerosol surfaces, it enhances the formation and growth of secondary organic aerosols[4]. The emission of BVOCs therefore indirectly affects the Earth's radiation balance, as secondary organic aerosols scatter solar radiation and act as cloud condensation nuclei, leading to enhanced albedo[5].

BVOC emission rates in general peak in the tropics and then decrease towards the poles[6]. In the Arctic, models have assumed minimal emissions due to low temperatures, short growing seasons and sparse vegetation cover[6,7]. However, recent field studies indicate that

emissions from arctic tundra greatly exceed estimates based upon models relying on ambient air temperatures rather than canopy temperatures[8,9], which are strongly decoupled from air temperature due to the low-stature canopy and adaptations of arctic plants ensuring maximal trapping of heat to warm the canopy[10,11].

Light is needed for photosynthesis, and BVOCs like isoprene that are directly released upon biosynthesis are emitted light-dependently[12]. The production and diffusion rates of BVOCs correlate with temperature, with typical exponential response curves[12]. Direct solar radiation has especially large influence on leaf temperatures in low canopy vegetation[11], such as tundra, and changes in cloud cover could thus indirectly have a large impact on emission rates.

While the effect of changes in light availability has hardly been considered, long term field studies suggest that BVOC emission response to experimental warming is much larger in high latitude compared to other ecosystems[13–16], indicating that the effect of climate changes on BVOC emission is dependent on the type and state of the ecosystem[16]. A potential reason for the large temperature response in high latitude systems is that the increased BVOC emission is an indirect result of temperature-driven plant biomass increase in these temperature-limited ecosystems[13]. The ongoing warming of the Arctic has led to increased plant biomass and altered species composition in the tundra[17], and experimental warming studies indicate that the biomass increase is linear over time[18].

In order to identify the mechanisms behind the large emission responses observed in the Arctic, we assessed the effects of warming (W) and reduced sunlight (RS) on BVOC emissions from arctic tundra separately for the whole ecosystem, dominant plants and soil. We examined the responses to elevated temperature using Plexiglas open top chambers, which increase air temperature by 2-3 °C, and to RS using dome-shaped hessian tents, which decrease photosynthetically active radiation (PAR) by 65%, in dry dwarf-shrub tundra in Western Greenland

(64°07’N, 51°21'W). The experiment had six replicate plots for each treatment. The vegetation was homogeneous and co-dominated by the crowberry *Empetrum hermaphroditum* and grey willow *Salix glauca* (Supplementary Table S1) with occasional spots of bare soil. Both plant species are common dwarf shrubs with a circumboreal-polar distribution.

The BVOC emissions were estimated using enclosure technique and collection of the emitted volatiles in adsorbent cartridges, which were analyzed by gas chromatography-mass spectrometry (see Methods). The ecosystem emissions were measured by enclosing whole ecosystem plots (33 × 33 cm) including intact vegetation and the underlain soil. The plant measurements were made on enclosed shoots of *E. hermaphroditum* and *S. glauca,* and the soil measurements were made on enclosed bare soil spots.

The unmanipulated heath proved to be a significant source of BVOCs having a daytime emission rate of 338 μg m^{-2} ground area h^{-1} averaged across the season (Fig. 1a). Isoprene, which was primarily emitted by *S. glauca,* dominated the emission profile constituting 87% of the total emission (Supplementary Tables S1 and S2). Non-terpenoid compounds accounted for 7% of the total emission, while sesquiterpenes and monoterpenes, primarily emitted by *E. hermaphroditum* (Supplementary Table S1 and S3), accounted for 5% and 1%, respectively. Across the season, the ecosystem BVOC emission was consistently higher from W and lower from the RS treatment compared to the control (Fig. 1a).

W increased the enclosure temperature by 3.1 °C averaged over all measurements (Supplementary Table S2), but it also decreased soil moisture from 22.0% in control to 17.8% in W (Supplementary Table S3). This decrease in soil moisture in response to warming is well in agreement with the projected changes in soil moisture under climate change[19]. The aboveground plant biomass was lower in both RS and W compared to the control (Supplementary Table 3S), and in order to not let this difference interact with the assessment of treatment effects on the emissions,

86 we proportioned the ecosystem emission to the estimated aboveground plant biomass in each plot
87 (see Methods). The decrease in aboveground plant biomass in W was in line with earlier findings
88 from water limited arctic ecosystems[17,18], and was likely due to amplified drought stress in the W
89 plots[11].

90 Proportioned to aboveground plant biomass, average ecosystem emissions increased
91 260% in W compared to the control (Fig. 2a). This temperature relationship corresponds to a Q10 of
92 22, in which Q10 describes the factor by which the emission rate increases with a 10 °C rise in
93 temperature. The high Q10 highlights the extreme temperature sensitivity of BVOC emissions from
94 arctic tundra relative to other processes affected by warming; for example, the Q10 for BVOC
95 emissions is typically between 3-6 (ref. 16), and that for biological processes in general is around
96 2.5 (ref. 20).

97 The ecosystem BVOC emission increase was primarily driven by isoprene and non-
98 terpenoid compounds, increasing 240% and 590% compared to the control, respectively (Fig. 2a).
99 The monoterpene and sesquiterpene emission response to warming was substantial but less
100 profound, with 140% and 60% increases in emissions, respectively. The effect of warming was
101 much greater than expected based on the parameterizations used in models applying exponential
102 relationships between emission rate and temperature[21] and more drastic than the increase
103 documented for a subarctic heath[14,22]. Furthermore, the effect was a consequence of direct
104 stimulation of biosynthesis, rather than a result of higher plant biomass due to warming[13]. The large
105 response to warming may be linked to the effects of decreased soil moisture, which is a key driver
106 of vegetation properties in arctic-alpine ecosystems[23]. Moderate drought stress has in some cases
107 increased isoprene emissions[15,16], possibly by limiting the naturally cooling evapotranspiration
108 process, resulting in higher leaf temperatures[11].

On average RS decreased PAR by 65%, air temperature in the enclosures by 5.7 °C (Supplementary Table S2) and soil temperature by 0.5 °C (Supplementary Table S3). Corrected for plant biomass, the total BVOC emission from RS was 69% lower than the control, mainly due to lower isoprene emissions (Fig. 2a). The decrease may be explained by the reduced temperature and probably to a higher extent by the light dependency of the emission of isoprene that is released upon synthesis, and thus coupled to photosynthesis[21,25].

The treatment responses in the plant shoot BVOC emissions were in agreement with the responses at the ecosystem level. Compared to the control, the total BVOC emissions from *S. glauca* and *E. hermaphroditum* increased with 90% in W, and decreased with 61-65% in RS (Fig. 2b and 2c). *S. glauca* had an average emission rate of 7.8 µg g^{-1} dw leaf biomass h^{-1} with isoprene accounting for 85% of the total emission (Fig. 2b). The average emission rate of *E. hermaphroditum* was 2.6 µg g^{-1} dw leaf biomass h^{-1}, mainly consisting of sesquiterpenes and non-terpenoid compounds (Fig. 2c).

In general, the emissions from bare soil proved to be substantial, constituting 20% of the total BVOCs released from the whole ecosystem measurements. Total soil BVOC emission rate was 59.1 µg m^{-2} h^{-1}, with non-terpenoid compounds accounting for 95%. The seasonal variation in soil and plant emissions is shown in Supplementary Figure S1, and complete lists of compounds emitted are shown in Supplementary Tables S4-S7.

The emission in RS was 78% lower than in the control (Fig. 2d), and thus it followed the negative response observed also in the plant and ecosystem measurements. However, in contrast to the stimulation of plant and ecosystem emissions, W had no effects on the soil emissions (Fig. 2d). The decrease in soil emissions by RS cannot be fully explained by abiotic factors since soil temperature at 3-5 cm depth only decreased by 0.5 °C (Supplementary Table S3), and solar radiation only directly affects the soil surface. Instead, we suggest that root biomass played a role.

The majority of BVOCs released from soil derive from the rhizosphere including emissions from roots, rhizospheric bacteria and fungi[26]. Reduced light availability increases allocation of resources to stem and leaves at the expense of roots[27] suggesting reduced biomass and thereby lower root-derived emissions in the RS treatment. Also the decrease in aboveground plant biomass in RS (Supplementary Table S3) has probably been accompanied by a decrease in root biomass. Results from an earlier long term warming experiment in arctic tundra indicate that belowground plant biomass is unaffected by open top chamber warming, which could explain the lacking soil emission response to warming in our study[28].

To assess which biological or environmental factors affect the ecosystem-level BVOC emissions, we conducted a partial least squares (PLS) regression[29] analysis on the ecosystem emission of the dominant BVOC, isoprene. Isoprene emission correlated positively with net ecosystem exchange, the biomass of *S. glauca*, a strong isoprene emitter[2], and PAR (Fig. 3) which is in agreement with the well-established light dependence of isoprene emission[12]. In contrast, several soil-related, inter-correlated, variables had a negative relationship with ecosystem isoprene emission (Fig. 3). The most influential of these variables were ecosystem respiration, soil microbial biomass carbon and bacterial abundance (number of 16S rDNA copies). We hypothesize that the negative relationship demonstrates active soil bacterial uptake of isoprene in the ecosystem[30]. The responses of this process to climate change and the importance to the ecosystem net emissions remain to be untangled.

Our results demonstrate several-fold increased BVOC emission from a dry arctic tundra heath in response to a realistic temperature increase mimicking projected warming in the Arctic[3]. The drastic increase is in agreement, but cannot be fully explained by increases in emissions per gram leaf biomass of the dominant plant species. The unexplained emission increase may be due to strong temperature dependency in BVOC emission from mosses, lichens,

decomposing litter and subdominant vascular plants in the whole ecosystem plots (Supplementary Table S1). Reduced sunlight decreased emission rates both from plants, soil, and the whole ecosystem, probably due to both reduced light availability *per se* and surface cooling.

Our results emphasize the increasing importance of BVOC emissions from the Arctic under climate change. Since 1979, arctic land surface has warmed at a rate of 0.5 °C per decade and in 2100 temperatures in the Arctic are projected to have increased by 2-8 °C (ref. 3). In remote areas, such as the Arctic, where the air is clean, the growth of particles large enough to act as cloud condensation nuclei, is tightly coupled to the emission of BVOCs[1], and warming-induced emissions in the Arctic may therefore lead to increased cloud formation. As BVOC emissions are highly regulated by sunlight availability, the warming-induced emissions might in fact initiate a negative feedback mechanism between the biosphere, aerosols and climate.

Additional Information

The processed data for this manuscript can be found in the Figshare database (http://figshare.com/authors/Magnus_Kramsh_j/830572).

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Author Contributions

MK and IVP collected the data. MK, IVP, MS and RR analyzed and interpreted the dataset. ÅR performed the PLS analysis. JN and HRP established the experimental site. MK wrote the manuscript with contributions from all authors.

Author Information

The authors declare no competing financial interests.

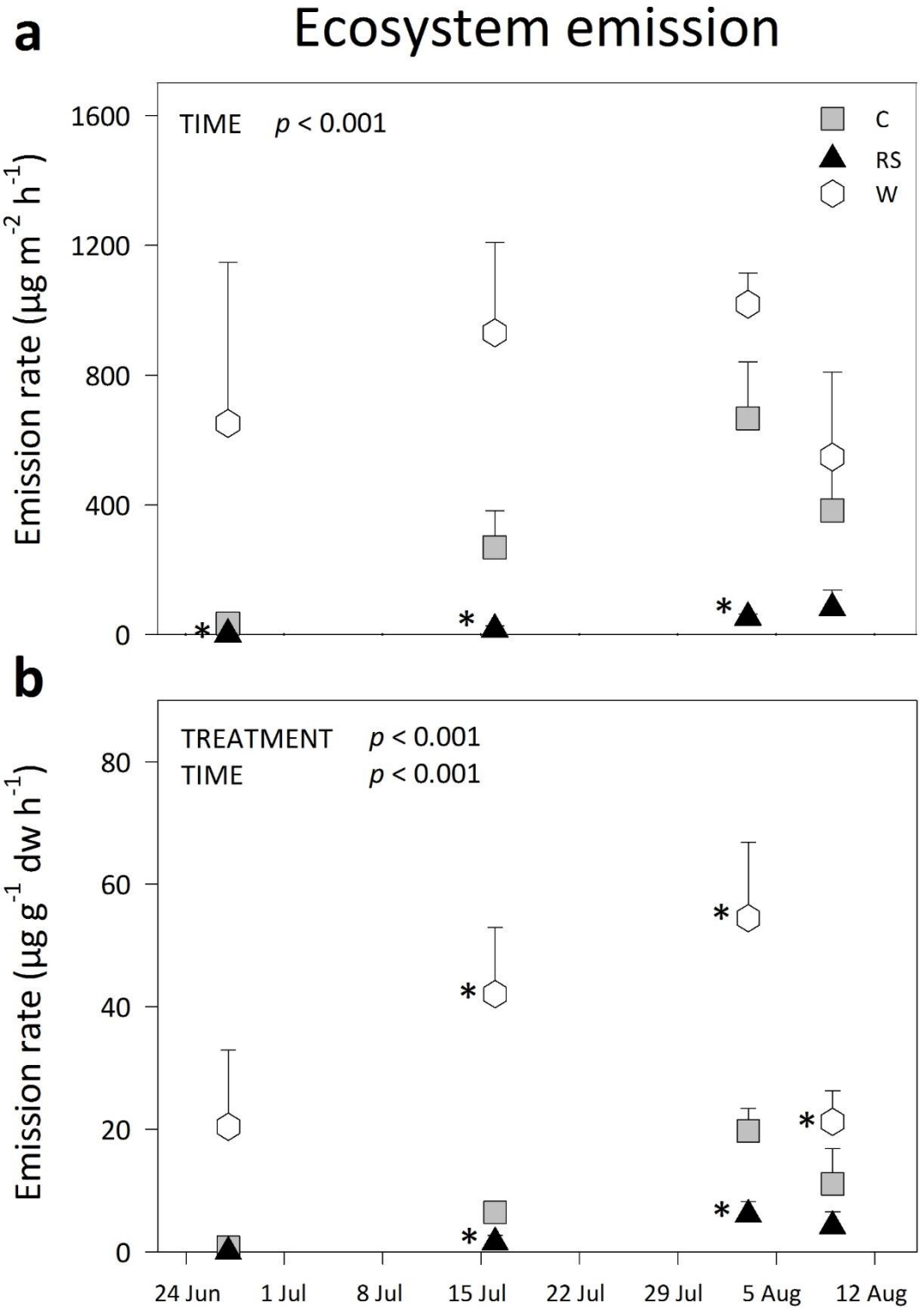


Figure 1: Biogenic volatile organic compound emission across the season. a, Mean emission rate (n = 5) per ground area and **b**, mean emission rate (n = 5) per dry weight plant biomass. Statistically significant p-values for the repeated measures ANOVA are shown. Asterisks signify

statistically significant difference from the control within the measurement dates (Dunnett's test, * $p < 0.05$). C, control; RS, reduced sunlight; W, warming. Error bars show standard error of the mean.

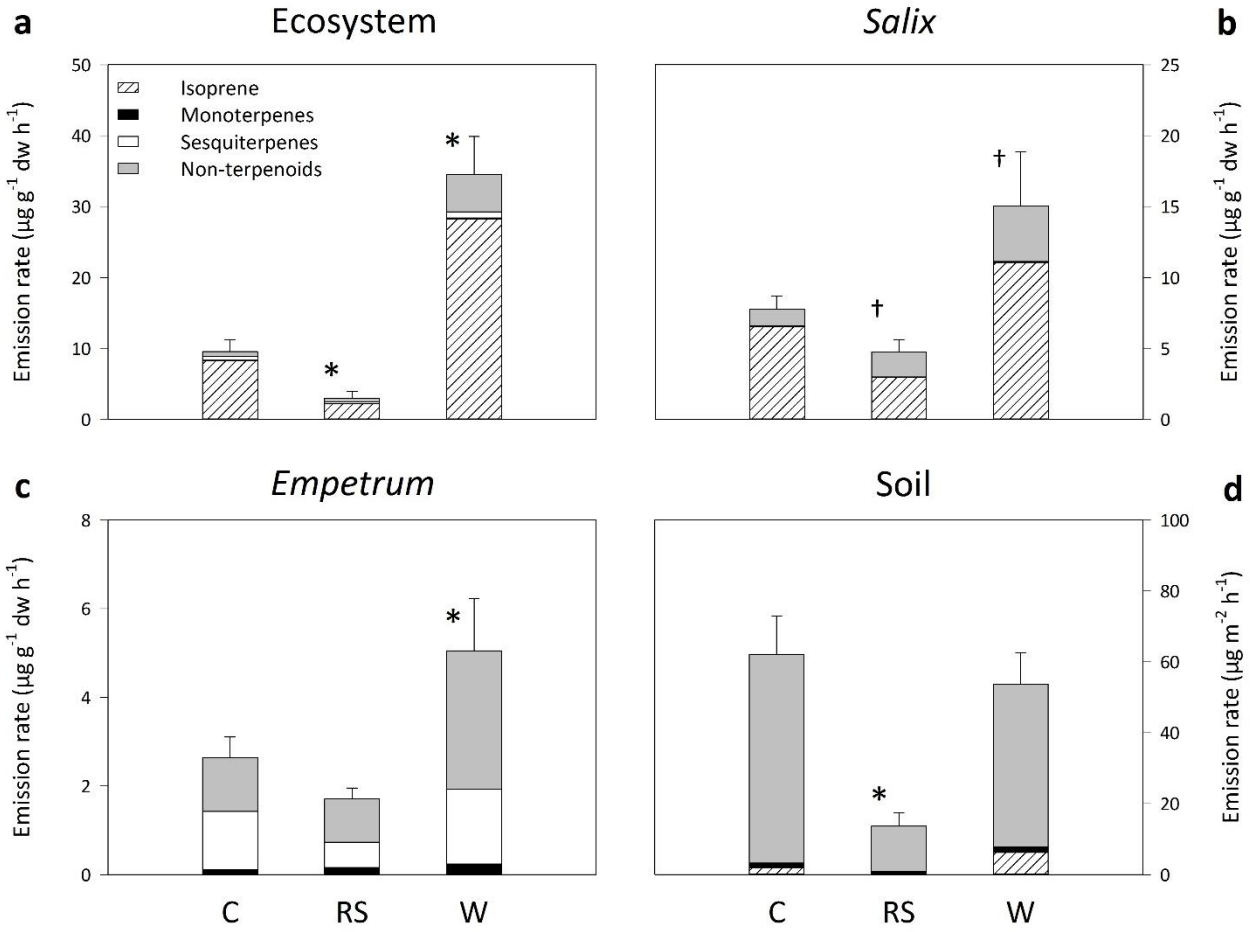
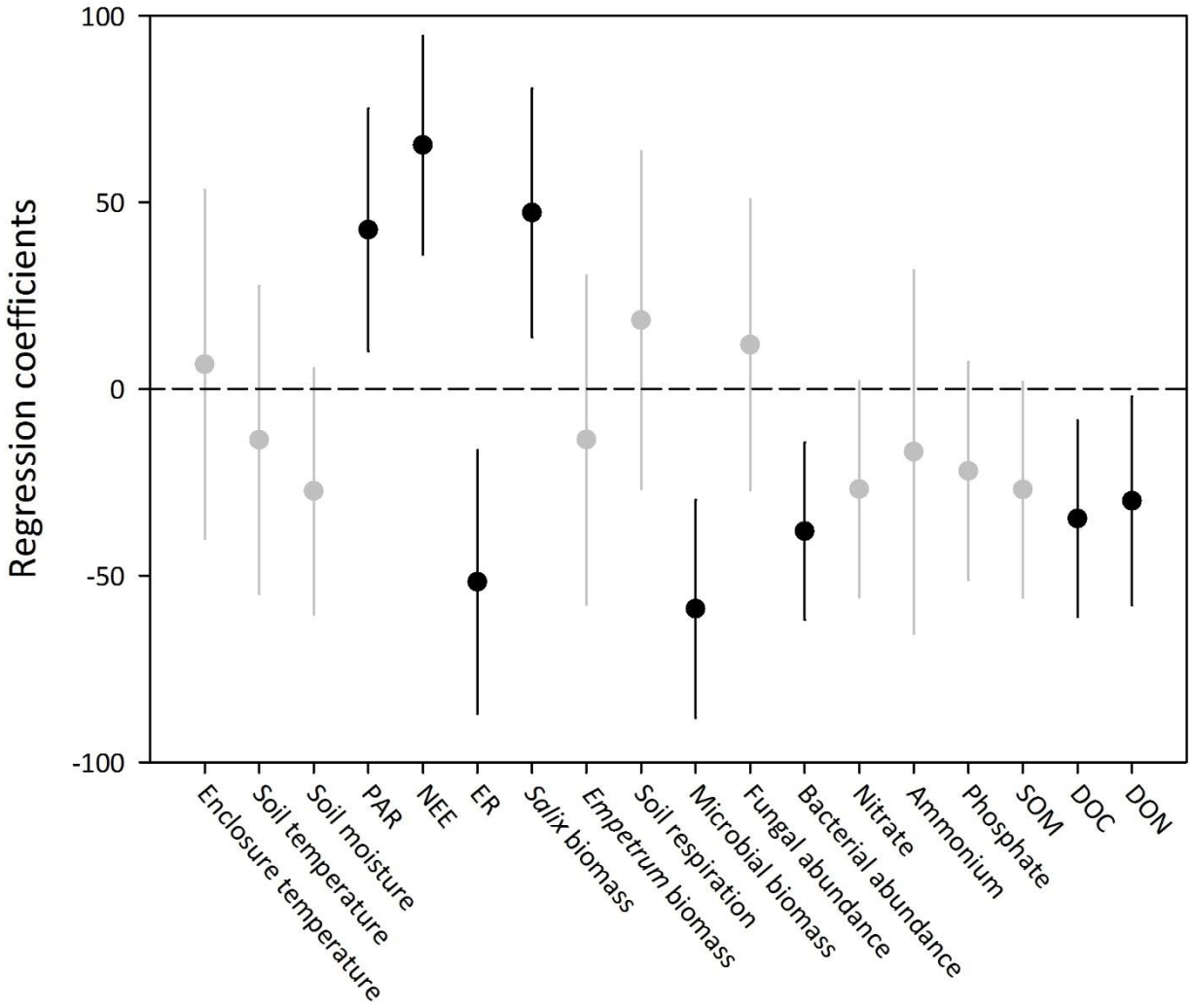


Figure 2: Growing season average of biogenic volatile organic compound emission. a, Emission from whole ecosystem corrected for plant biomass ($n = 5$) **b**, Emission from *Salix glauca* ($n = 6$) **c**, Emission from *Empetrum hermaphroditum* ($n = 6$) and **d**, Emission from soil ($n = 6$). The division of the total emissions to isoprene, monoterpenes, sesquiterpenes and non-terpenoids is shown. Symbols signify statistically significant difference compared to control (Mixed model, Dunnett's test, * $p < 0.05$; † $p < 0.1$). Error bars represent standard error of the mean.



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299 **Figure 3: Correlation between measured background variables and isoprene emission for the**
300 **tundra ecosystem.** Average regression coefficients for the partial least squares regression on
301 isoprene emission. The error bars show 1.96 × standard error calculated from 1000 bootstrap
302 samples. Significant factors are shown in black. PAR, photosynthetically active radiation; NEE, net
303 ecosystem exchange; ER, ecosystem respiration; SOM, soil organic matter; DOC, dissolved organic
304 carbon; DON, dissolved organic nitrogen.

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Methods

Study site and experimental setup

The data were collected during the growing season of 2013 in Kobbefjord, 20 km southeast of Nuuk, Greenland (64°07'N, 51°21'W). The experiment that was initiated in 2007 (ref. 31) spanned approx. 50 x 100 m and consisted of 18 hexagon-shaped plots (diameter 1.2 m). Control plots and the treatments W and RS were distributed to the experiment in randomized complete block design (n = 6). One block was excluded from the "whole ecosystem" measurements, because the vegetation composition in this block differed from the other blocks. It did not have any *Salix glauca*, which was one of the two dominant species in the studied tundra (n = 5).

Sampling of BVOCs

Plant and soil BVOC emission was measured using a dynamic headspace sampling technique, while ecosystem emission was measured using a push-pull enclosure technique[13,32]. Air was circulated through the systems by battery-operated pumps connected via Teflon tubes. The incoming air was purified by an activated charcoal filter to remove particles and VOCs, and by a MnO_2 scrubber to remove ozone[33]. Air was pumped out of the enclosures through stainless steel adsorbent cartridges containing 150 mg Tenax TA and 200 mg Carbograph 1TD (Markes International Limited, Llantrisant, UK) at 200 ml min^{-1}. Following the 30 minute long sampling, the adsorbent cartridges were sealed with Teflon-coated brass caps, and stored refrigerated until analysis. The used adsorbent cartridges capture compounds in the range C5-C30. Using this method a number of oxygenated BVOCs might not be captured quantitatively.

We used precleaned (120 °C for 1 hr.) disposable polyethylene terephthalate (PET) bags that were attached to a polyvinyl chloride (PVC) cylinder (diameter 10 cm) installed in bare

soil or around a shoot of *S. glauca* or *E. hermaphroditum*, for soil and plant enclosures, respectively. The adsorbent cartridge was inserted into the PET bag through a hole cut in the corner, which was afterwards tightly closed with plastic-coated wire. Prior to each measurement, the bags were ventilated for five minutes with an inflow rate of 1000 ml min^{-1}, and during measurements the inflow was set to 500 ml min^{-1}. For ecosystem enclosures, a transparent polycarbonate chamber (25 L; Vink Finland, Kerava, Finland), equipped with a fan to ensure well-mixed headspace, was placed on the permanent chamber base in each plot. The cartridge was mounted directly on the chamber and the inflow rate was set to 215 ml min^{-1}.

Blank samples were collected to account for VOCs released from sampling materials or analysis system. During all measurements, shaded iButtons (Hygrochron, Maxim Integrated, San Jose, USA) placed inside the enclosure logged temperature and relative humidity once per minute. PAR was monitored in each treatment using S-LIA-M003 sensors connected to a HOBO micro station data logger (H21-002, Onset computers corporation, Boston, USA).

Analysis of BVOCs

The BVOC samples were analyzed by a gas chromatograph-mass spectrometer (7890A Series GC coupled with a 5975C inert MSD/DS Performance Turbo EI System, Agilent, Santa Clara, CA, USA) after thermal desorption (UNITY2 coupled with an ULTRA autosampler, Markes, Llantrisant, UK). The carrier gas was helium and oven temperature was held at 40 °C for 1 min, then raised to 210 °C at a rate of 5 °C min^{-1}, and finally further to 250 °C at a rate of 20 °C min^{-1}. BVOCs were separated using an HP-5 capillary column (50 m, diameter 0.2 mm, film thickness 0.33 µm).

BVOCs were identified using pure standards and according to their mass spectra in the NIST 8.0 mass spectral data library, and quantified with pure standards (see Supplementary

Table S8 for a list of compounds). Standard solutions were injected into adsorbent cartridges in a stream of Helium and analyzed as samples. When quantifying compounds for which no pure standard was available, α-pinene was used for monoterpenes, humulene was used for sesquiterpenes and toluene was used for non-terpenoids. Compounds were classified into one of following four groups: isoprene, monoterpenes, sesquiterpenes and non-terpenoids.

The plant emissions were calculated on leaf dry weight basis, soil emissions on ground area basis, and ecosystem emissions both on ground area basis and per dry weight estimated aboveground plant biomass in each plot. All emission rates are reported as actual, not normalized, emissions.

Vegetation analysis and estimation of plant biomass

The vegetation cover of vascular plants, mosses, lichens and litter was estimated in the plots subjected to ecosystem-level BVOC emission measurements and in 21 additional plots adjacent to the field experiment. The analysis was conducted in mid-July by the point intercept method using a 35 x 35 cm frame with 25 fixed points[34]. In the additional plots, the vegetation was harvested, oven dried (60 °C for 72 hrs.) and weighed. For each species, linear regression was used to model the biomass in the experimental plots, based on the point intercept data.

Ecosystem emission per gram plant biomass

Isoprene emission was calculated per gram *S. glauca* present in each plot, monoterpene and sesquiterpene emission was calculated per gram biomass of all vascular plants except *S. glauca* and the emission of non-terpenoid compounds was calculated per gram total plant biomass.

Q10-value for ecosystem emission

Q10 was calculated using the following formula:

$$Q10 = \frac{E_W}{E_C}^{10/(T_W - T_C)}$$

where E_W is the average ecosystem BVOC emission rate in the warmed plots and *Ec* is the average ecosystem BVOC emission rate in the controls. T_W is the average temperature inside the enclosures in the warmed plots and T_C is the average temperature inside the enclosures in the controls.

Background data

In each plot, soil temperature at 3-5 cm depth was monitored every hour using M-Log 5W Wireless Temperature Data Loggers (Geoprecision, Ettlingen, Germany). Soil moisture was measured once a week during the entire growing season.

Net ecosystem exchange, ecosystem respiration and soil respiration were measured weekly with a LI-6400XT portable gas-analyzer (LI-COR, Biosciences, Lincoln, USA; see Haugwitz et al. paper in preparation). The concentrations of dissolved organic nitrogen, ammonium, nitrate and phosphate in the soil were determined in ddH_2O-extracts of fresh soil using spectrophotometry (see Haugwitz et al. paper in preparation). Dissolved organic carbon (DOC) was analyzed with a Shimadzu TOC-L CSH/CSN^{TM} total organic carbon analyzer (Shimadzu, Kyoto, Japan), and microbial biomass was estimated from the difference in the DOC concentration in the chloroform-fumigated and non-fumigated samples[35]. DNA was extracted from freeze-dried soil using FastDNA^{TM} Spin Kit for Soil, and subsequently quantitative polymerase chain reaction was performed targeting ITS2 region and 16S rDNA to estimate the fungal and bacterial abundance in the soil (see Haugwitz et al. paper in preparation).

Statistical tests

The treatment effects on BVOC emissions in repeated measurements were tested by a linear mixed model in SAS 9.2. including Treatment (three levels: Control, W and RS) and Time as fixed factors and Block as a random factor. Interactions with *p*-values > 0.2 were stepwise removed from the model. One-way ANOVA was used to test for treatment effects within each measurement and for growing season averages. A Dunnett's test was used as a post hoc test to compare each treatment to the control. The effects of biological and environmental factors on the ecosystem-level isoprene emission were assessed by the PLS analysis. The tested variables, measured in the same plot, included enclosure temperature, soil temperature, soil moisture, PAR, *S. glauca* biomass and *E. hermaphroditum* biomass described in the present study and net ecosystem exchange, ecosystem respiration, soil respiration, microbial biomass, fungal and bacterial abundance, nitrate, ammonium, phosphate, soil organic matter, dissolved organic carbon and dissolved organic nitrogen (see Haugwitz et al. paper in preparation). The PLS was performed with a cross-validation with six segments in a Venetian blinds according to isoprene emission. In order to estimate the uncertainty in the regression coefficients of each of the factors a resampling scheme – bootstrapping[36] – was performed 1000 times. One component PLS models were used throughout the analysis, and the standard error was calculated as given in Wehrens et al. (ref. 36).

Method references

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